



Catalytic abatement of styrene traces in polystyrene: A model study of styrene reaction with excess cumene

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ABSTRACT

The conversion of styrene in the presence of cumene has been studied on a family of aluminosilicate acid catalysts. This study was part of a project aimed at the removal of styrene monomer traces in polystyrene (PS). The catalytic experiments were performed at 200 °C in a closed stirred tank reactor with 1.92 mmol styrene, 49.8 mmol cumene and 60 mL *n*-dodecane as solvent. The evaluated catalytic materials were faujasite and beta zeolites, and amorphous silica-aluminas with disordered or ordered mesoporosity. Four reaction paths are involved in the styrene conversion. A free-radical chain polymerization in the homogeneous phase is mostly sensitive in the presence of catalysts of low activity. The three other transformation routes are catalyzed by the acid sites of the materials: (1) hydrogen transfer between styrene and cumene to ethylbenzene and α -methylstyrene; (2) ring oligomerization of styrene to dimers and trimers; (3) alkylation of cumene by styrene into primary and secondary alkylates. The presence of acid sites is a prerequisite for the styrene transformation to occur on the materials. However, the key factor for the catalytic activity is the presence of a large mesoporous volume favoring the molecular traffic within the solid. Mesoporous silica-aluminas behave most favorably in this sense. As regards the distribution of products, a strong acid strength as well as the increase of the cumene/styrene molar ratio favor the alkylation pathway. There is a dark coloration of the reaction medium when carbocations are trapped within the micropores of zeolites. Among the catalysts investigated, the most attractive materials as regards activity, selectivity and a coloration of the solution are mesoporous silica-aluminas and, more preferably, those featuring an ordered porosity of the MCM-41 type.

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1. Introduction

Polystyrene (PS) is a thermoplastic with a broad spectrum of properties which make it one of the most useful plastics used in different common facility products such as cups, food containers, toys, home furniture, building materials, etc. However, a serious concern in the PS manufacture is the removal of residual materials which can migrate out of the polymer upon use. The principal classes of substances which can migrate from polystyrene are residual styrene monomers and low molecular weight oligomers, since the free-radical bulk polymerization manufacturing process is not 100% efficient. Migration of styrene to foodstuff is of special concern as it may present a health hazard to the consumer or cause unacceptable changes to the organoleptic properties of food and

beverage. The styrene content in PS for general application does not exceed 1000 ppm and generally ranges from 200 to 400 ppm for foodstuff packaging PS. Styrene is classified in EPQ's Toxic Release Inventory as a carcinogen but still listed without any restriction in the directive 90/128/EEC assessed by the European Scientific Committee on Food. However, it is expected that more stringent regulations regarding foodstuff packaging will appear in the very next future, asking for styrene contents well below 100 ppm.

The best available technologies for finishing treatment of PS (heat and vacuum stripping) allow to decrease the styrene content to ca 200 ppm but are ineffective to fall below 100 ppm in economically acceptable conditions. New concepts for PS treatment are thus needed to reach this goal. Recent patents claim that the treatment at ca 200 °C of PS with small amounts of an inorganic acid material decreases the styrene content to an extent which depends on the material used [1,2]. A non-exhaustive list of the materials claimed to be effective in the process includes various zeolites and amorphous silica-aluminas. In the process, the material is added as a sacrificial catalyst (0.25–1.0 wt%) in the molten PS at about 200 °C

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Table 1
Some characteristics of the catalysts.

Catalyst	Si/Al	Micropores		Mesopores		Acidity ^a (mequiv. g ⁻¹)
		Average diameter (nm)	Volume (mL g ⁻¹)	Average diameter (nm)	Volume (mL g ⁻¹)	
BEA(12)	12	0.6	0.22	4.5	0.22	1.20
BEA(22)	22	0.6	0.16	6.2	0.14	0.95
FAU(2.5)	2.5	0.7	0.31	–	–	1.95
FAU(15)	15	0.9	0.28	2.1	0.10	0.55
MCM-41(4)	23	–	–	3.8	0.74	0.30
MCM-41(5)	18	–	–	5.2	0.76	0.30
MCM-41(7)	22	–	–	6.7	0.60	0.30
Davicat2013	41	1.3	0.06	2.4	0.35	0.20

^a Acidity characterized by the amount (mmol g⁻¹) of NH₃ desorbed in NH₃-TPD experiments.

in the extruder to promote styrene oligomerization and/or alkylation of styrene on PS. However, two negative aspects need to be controlled: the formation of ethylbenzene, and the coloration of PS (from pale yellow to brownish). The former phenomenon may be due to hydride transfer and the latter to the sequestration of carbocations within the catalyst porosity. Most promising sacrificial catalysts were beta-type zeolites, amorphous silica-aluminas and ordered mesoporous silica-aluminas of the MCM-41-type.

With the aim of designing an optimised catalyst through the understanding of the main reactions involved in the process, we have undertaken a basic study of the reaction of cumene with styrene as a very simplified model of the catalytic transformation of styrene traces in PS. Cumene was chosen for two main reasons: (a) its carbon skeleton corresponds to the shortest unit of PS containing a tertiary carbon atom; (b) it should allow an easier analysis of the reaction medium. The catalytic alkylation of cumene with styrene has been scarcely studied. Shoko and Togami [3] claimed that various zeolites including zeolite Y, USY, mordenite, ZSM-5 and ZSM-12 are effective in cumene alkylation by styrene to prepare a solvent containing a high proportion of 1-phenyl-1-(isopropylphenyl)ethane.

The aim of the present work was to identify the reaction pathways involved in the catalytic transformation of styrene in the presence of cumene under experimental conditions close to those of a real finishing treatment of PS and to discuss the influence of the physico-chemical characteristics of the catalysts on the process.

2. Experimental

2.1. Materials

The zeolite materials used as catalysts belong to the class of large-pore zeolites (i.e. zeolite topologies with pore openings consisting of rings of 12 tetrahedra): zeolite Y (FAU) from UOP and PQ and zeolite beta (BEA) from PQ. Two types of mesoporous amorphous silica-aluminas (ASA) were used: a commercial material featuring 2 nm pore size (Davicat 2013, Grace Davison) and three homemade templated silica-alumina solids with ordered porosity of the MCM-41 type [4].

2.2. Characterization

The textural and acidic properties of the catalysts were determined by nitrogen sorption at 77 K and temperature-programmed desorption of ammonia (NH₃-TPD), respectively.

The nitrogen adsorption–desorption isotherms on the samples calcined at 773 K were determined with a Micromeritics ASAP 2100 instrument at 77 K. The micropore (pore diameter <2 nm) and mesopore (pore diameter 2–50 nm) volume were determined by the t-plot method. Pore size was determined by the DFT method.

The total acidity was measured by NH₃-TPD experiments. The samples were previously outgassed at 773 K, cooled to 373 K and

contacted with NH₃ stream (purity >99.5%). After purging for 7 h with a He stream (purity >99.995%, flow = 30 cm³ min⁻¹), the temperature was increased up to 773 K (ramp = 10 K min⁻¹). The desorbed NH₃ was neutralized with a HCl solution and titrated by conductimetry.

The characteristics of the catalysts are given in Table 1.

2.3. Catalytic experiments

The catalytic efficiency of the materials was evaluated in a batch reactor (100 mL) containing 1.92 mmol styrene, 49.8 mmol cumene, and 1.92 mmol *n*-decane (internal standard) in 60 mL *n*-dodecane solvent. Experiments with different amounts of reagents were carried out as further described for sake of mechanism identification. The activated (550 °C in flowing air) and freshly dehydrated (120 °C, overnight) catalyst (100 mg) was poured into the reaction mixture and after closing and purging the reactor with nitrogen, the reaction temperature was raised up to 200 °C in 10 min. The time zero of the reaction onset was taken when the reaction temperature was reached.

The progress of the transformation was followed by gas chromatography analysis (Varian 390, equipped with a capillary column CPSil 5CB, 15 m, 0.25 mm). Identification of the main products was carried out by GC-MS coupling on a HP 5970 apparatus equipped with the same column.

The catalytic behavior of the materials was characterized by the styrene conversion and the yield in products:

$$\text{styrene conversion} = \frac{[\text{styrene}]_0 - [\text{styrene}]_t}{[\text{styrene}]_0}$$

where [styrene]₀ and [styrene]_t are the initial concentration of styrene, and at time *t*, respectively

$$\text{yield}_i = \frac{[\text{product}_i]_t \times n}{[\text{styrene}]_0 - [\text{styrene}]_t}$$

where *n* is the number of styrene molecules engaged in the formation of product *i*.

3. Results and discussion

3.1. Preliminary study

3.1.1. Blank experiments

Because many possibilities of reaction pathways between the chemicals present in the medium exist, a series of preliminary experiments with and without a catalysts were carried out in order to better describe the formal reaction scheme

In the absence of catalyst (styrene + cumene + solvent, Fig. 1a, blank), styrene is consumed via a free-radical polymerization mechanism (Scheme 1). Neither volatile nor light products (dimers and trimers) are detected suggesting that the reaction leads to

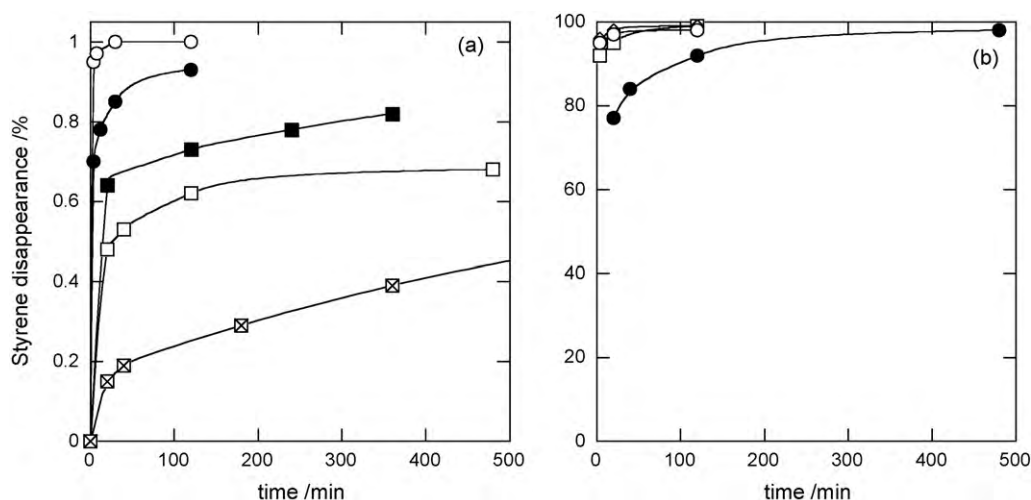
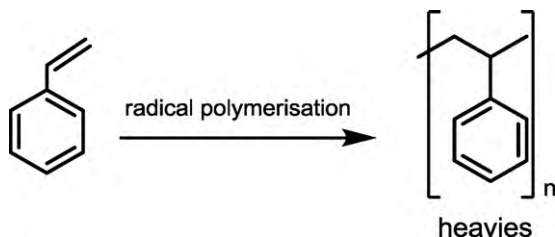


Fig. 1. Disappearance of styrene as a function of time. (a) On zeolites: (○) BEA(12), (●) BEA(22), (□) FAU(2.5), and (■) FAU(15). (b) On silica-alumina: (●) Davicat 2013, (□) MCM-41(3.5), (◇) MCM-41(5), (○) MCM-41(7); (⊠) blank experiment.



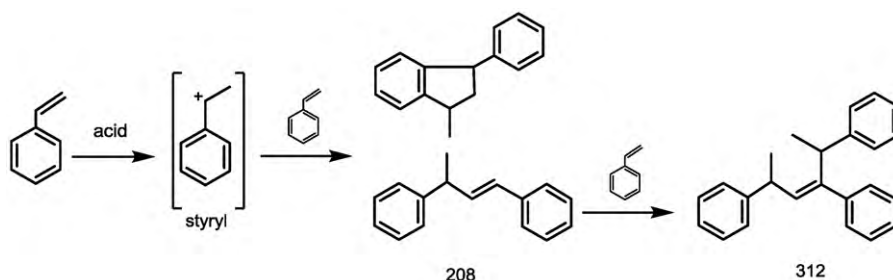
Scheme 1. Radical-assisted oligomerization of styrene to heavies ($n > 3$).

a short-chain polystyrene moiety (hereafter denominated “heavies”). The polymerization rate is high initially, during the first 20 min, then decreases, in agreement with the increase in chain length of the growing polymer.

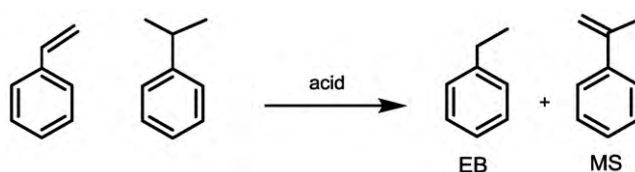
In the presence of a solid without any acid site (styrene + cumene + solvent + silica), the styrene conversion superimposes with the blank experiment. This provides evidence that disappearance of styrene by adsorption on the material is marginal in the process.

3.1.2. Products and pathways identification

In the presence of a solid acid catalyst (MCM-41(5)) neither dodecane nor cumene react under the experimental conditions. The reaction of styrene alone (1.92 mmol in 60 mL dodecane solvent) is very rapid and leads, after 10 min reaction, to a mixture of dimers ($m/e = 208$) and trimers ($m/e = 312$) via an acid-catalyzed oligomerization process (Scheme 2). This is in agreement for the dimerization of styrene catalyzed by solid acid catalysts [5].



Scheme 2. Acid-catalyzed dimerization and trimerization of styrene.



Scheme 3. Formation of ethylbenzene and α -methylstyrene by hydrogen transfer reaction between styrene and cumene.

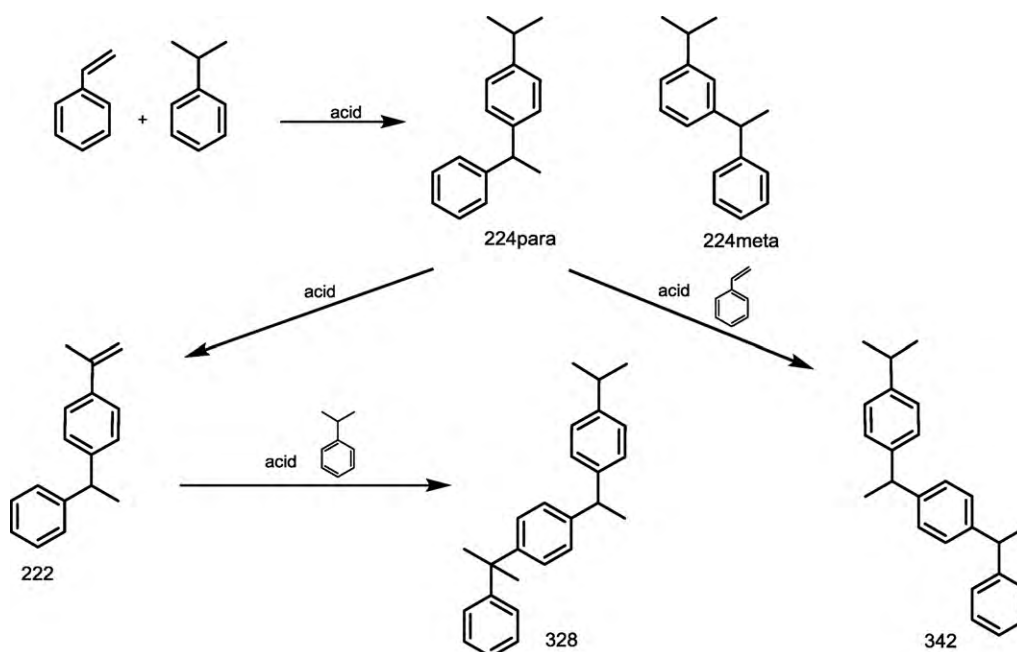
The addition of cumene to the reaction medium (1.92 mmol styrene, 49.8 mmol cumene, 60 mL *n*-dodecane solvent) reveals two additional routes for the transformation of the styryl carbocations:

- Hydrogen transfer leading to ethylbenzene (EB) and α -methylstyrene (MS) (Scheme 3) (Note that under the experimental conditions applied, i.e. in the absence of metal and hydrogen, no direct hydrogenation of styrene into EB occurs).
- Alkylation into a family of products identified as primary ($m/e = 224$) and secondary ($m/e = 222, 328, 342$) products, hereafter denominated “alkylates” (Scheme 4).

On the bases of this preliminary study, the overall reaction pathway for the reaction of styrene is summarized in Scheme 5.

3.2. Influence of the nature of the catalyst on reactivity

The conversion of styrene as a function of time over the eight solid acid catalysts is shown in Fig. 1. The product distributions



Scheme 4. Acid-catalyzed alkylation of cumene with styrene and some secondary alkylates products.

obtained at the end of the corresponding runs are detailed in Table 2.

With the exception of the two faujasite zeolites, the catalysts demonstrated high activity in converting styrene, with over 85% conversion achieved after a few minutes. Among the solids investigated BEA(12) and the MCM-41 type catalysts allowed a quantitative transformation of styrene in ca 5 min reaction. Product distributions obtained over the various solids differed however significantly (Table 1), highlighting unique behaviors for the two families of catalysts.

The production of heavies, via the free-radical mechanism (Scheme 5) is clearly higher for the catalysts of low activity. Indeed, the most active catalysts, BEA(12) within the zeolite family and all four ASA (Fig. 1), produce the lower amounts of heavies. Such a behavior is in line with competitive kinetics between the free-radical reaction in the liquid phase (Scheme 5, path I) and the acidic catalyzed pathway (Scheme 5, path II) occurring on the surface of the solid acid.

As regards the reactions occurring on the catalyst surface, the oligomerization and alkylation routes (Scheme 5, paths III and IV) proceed with similar rates on zeolites (III/IV = 1–2) whereas oligomerization is significantly favored over the silica-aluminas (III/IV = 4–5). The extent of hydrogen transfer leading to ethylbenzene is less sensitive to the catalyst type. The ratio EB/MS, higher than unity, is consistent with the higher reactivity of

α -methylstyrene which undergoes secondary alkylation and or oligomerization reactions.

The color of the reaction medium at the end of the catalytic tests appears catalyst sensitive too, the ASA catalysts leading qualitatively to less intense coloration.

The high efficiency of the ASA catalysts compared to zeolites for the catalytic conversion of styrene, witnessed by the low rate of production of heavies via a competing free-radical mechanism, cannot be related to their acidity as zeolites exhibit a much larger and stronger density of acid sites than ASAs as illustrated in Fig. 2. All the materials show a distribution of acid sites, characterized by a broad range of desorption temperature in the NH_3 -TPD thermograms, but the number (total intensity of the envelope signal) and the strength (position of the maxima) of the sites is definitely higher on zeolites. The most straightforward explanation accounting for the observed results stands in the textural characteristics of the two types of catalysts. The four ASA materials investigated exhibit disordered (Davicat2013) or ordered (MCM-41) mesopores with openings larger than 2 nm. Their active acidic surface is fully available for styrene adsorption and activation via the formation of intermediate styryl cations, preventing its reaction via a free-radical mechanism. We can therefore reasonably propose that mesopores larger than 2 nm favor the adsorption of the reactants and the molecular traffic to and from the active sites of the bulky products of the styrene transformation (Schemes 2–4), and conse-

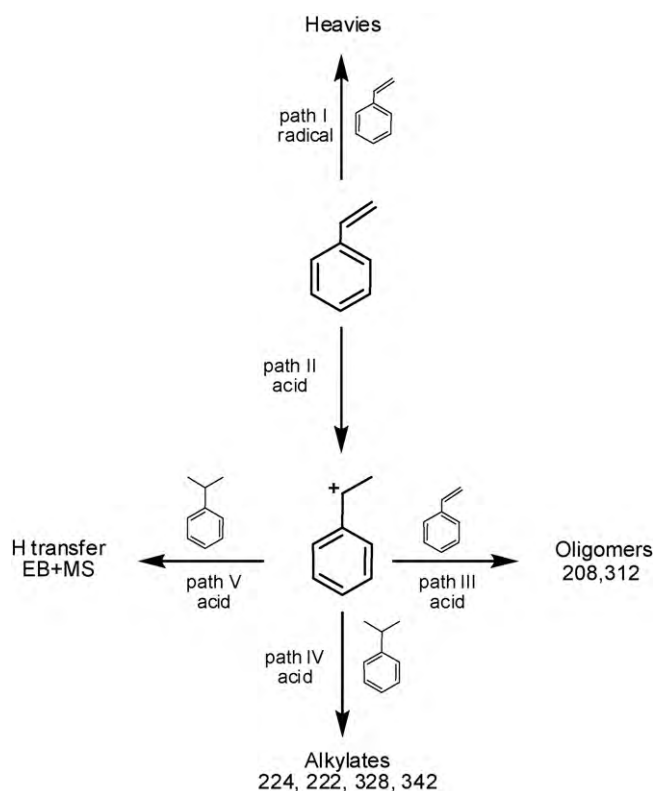
Table 2

Distribution of styrene-containing products at high conversion in the reaction of styrene and cumene on zeolites and silica-alumina.

Catalyst	Styrene conversion/%	Yield ^a (%)				EB/MS ^b	Color of the reaction medium
		Alkylates	Dimers + trimers	Heavies	EB		
BEA(12)	98	34	45	13	6	3.5	Brown
BEA(22)	93	33	37	20	3	1.5	Dark brown
FAU(2.5)	68	9.5	20	32	6	1.5	Black
FAU(15)	78	15	25	30	8	2	Black
MCM-41(4)	99	16	80	1	3.5	1.5	Light tan
MCM-41(5)	99	19	74	1	5.5	1.9	Light brown
MCM-41(7)	98	17	67	8	6.0	1.1	Light brown
Davicat2013	98	17	63	12	5.5	1.3	Tan

^a Calculated with respect to converted styrene.

^b Molar ratio in product.



Scheme 5. Simplified representation of the different pathways for styrene conversion.

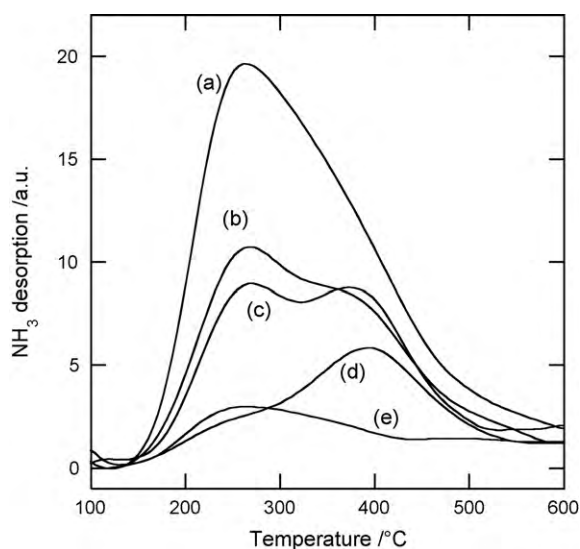


Fig. 2. Temperature programmed desorption of NH_3 from the various aluminosilicates: (a) FAU(2.5), (b) BEA(12), (c) BEA(22), (d) FAU(15), and (e) MCM-41(5).

quently the efficiency of the catalytic process. It is interesting to note that even for the zeolite catalysts the presence of a secondary network of mesopores has a definite effect on activity. BEA(12), BEA(22) and FAU(15) exhibit some mesopore volume and are the most active zeolite catalysts too. Mesopores in zeolite materials originate from defects created upon dealumination (FAU(15)) [6] or from the aggregation of nanocrystals (BEA(12) and BEA(22)) [7].

An influence of the acidity characteristics of the catalysts, and more precisely of the strength of the sites, can nevertheless be noticed when considering the products selectivities. As said above, the relative amounts of alkylates is systematically higher when using zeolites than with the ASA catalysts. FTIR and kinetic studies of the reaction of styrene and toluene [8] in liquid phase on silica-zirconia supported heteropoly acid catalysts shows that the carbenium ion mechanism (acid-catalyzed) involves the reaction of an adsorbed, activated, styrene with toluene or with a second styrene molecule. The orientation of the reaction depends on the relative coverage of the two competing reagents. Increasing the density and strength of the acid sites favors the retention of a higher fraction of toluene, and accordingly, a higher yield in alkylates. The higher selectivity into alkylates among the products formed via the acid-catalyzed route in our case can be well understood on the bases of the stronger acidity of the zeolites. In addition, though not totally elucidated, the origin of the coloration of the final mixture (PS in pilot scale experiments [1], reaction medium in this study) has been ascribed to the retention of carbocationic residues within the pores or at the surface of the catalysts. The presence of very strong acid sites on the zeolite catalysts could contribute to the stabilization of such charged species and negatively impact the overall process regarding the coloration of the reaction medium.

To complete this study we have carried out a supplementary experiment: the conversion of styrene in the presence of a large excess of cumene (cumene/styrene = 280 mol/mol) without solvent, using one of the most attractive catalyst, i.e. MCM-41(5). This experiment may mimic the actual reactivity of styrene in molten PS. The conversion of styrene reaches 96% after 4 min reaction. At the end of the run the products distribute into 45% alkylates, 36% oligomers, 11% ethylbenzene and 8% heavies. By comparison with experiments described above in the presence of *n*-dodecane solvent and with a cumene/styrene ratio of 26, a larger excess of cumene strongly favors the alkylation reaction with respect to oligomerization, on account of the respective surface coverage in both reactants. The same trend should prevail during the conversion of styrene in molten PS: a grafting of styrene on the PS chain rather than its oligomerization would be expected.

In final, and as regards a process designed to remove the styrene traces from a polystyrene melt, it turns out that the best catalyst candidate should combine a large surface area accessible through pores larger than 2 nm and a moderate acidity, both in terms of density and strength of the sites. It is worthy to note that the highest removal of styrene traces (from 180 down to 46 ppm) associated with low ethylbenzene formation and a very pale coloration of the PS granulates was claimed with a MCM-41 type material [1].

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